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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

FROOM et al

Serial No. 09/752,834

Filed: January 3, 2001

For: ESTER SYNTHESIS



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Examiner:

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March 19, 2001

Assistant Commissioner for Patents
Washington, DC 20231

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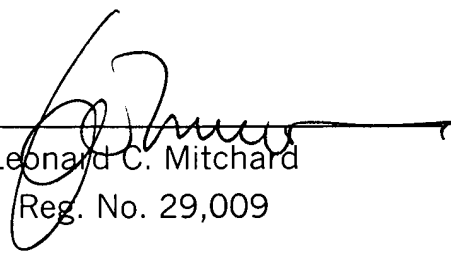
It is respectfully requested that this application be given the benefit of the foreign filing date under the provisions of 35 U.S.C. §119 of the following, a certified copy of which is submitted herewith:

<u>Application No.</u>	<u>Country of Origin</u>	<u>Filed</u>
9815135.0	Great Britain	14 July 1998

Respectfully submitted,

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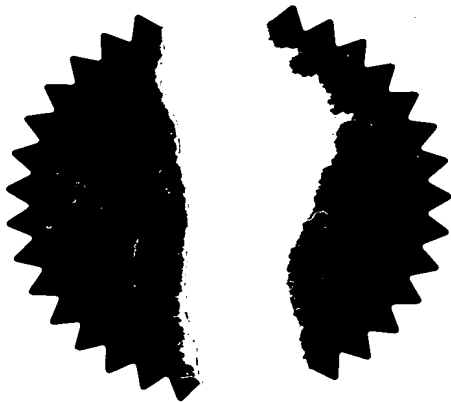
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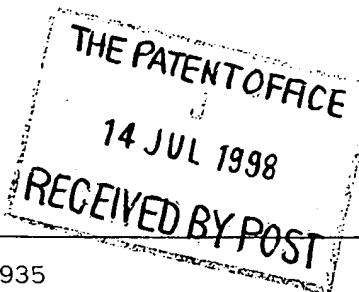
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Signed *Andrew Gersey*
Dated 10 January 2001

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14JUL98 E375306-1 C03022
 P01/7700 25.00 - 9815135.0

The Patent Office

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14 JUL 1998

1. Your reference

8935

2. Patent application number

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9815135.0

3. Full name, address and postcode of the or of each applicant (underline all surnames)

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Patents ADP number (if you know it)

L141591002

If the applicant is a corporate body, give the country/state of its incorporation

ENGLAND, UNITED KINGDOM

4. Title of the invention

ESTER SYNTHESIS

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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 MIDDLESEX
 TW16 7LN

Patents ADP number (if you know it)

B653925001

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Country

Priority application number
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Date of filing
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Number of earlier application

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Signature

KRISHNAN, Suryanarayana Kalyana

Date 13.07.1998

12. Name and daytime telephone number of person to contact in the United Kingdom 01932 762734

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ESTER SYNTHESIS

The present invention relates to a process for the synthesis of esters by reacting an olefin with a lower carboxylic acid in the presence of an acidic catalyst.

It is well known that olefins can be reacted with lower aliphatic carboxylic acids to form the corresponding esters. One such method is described in GB-A-
5 1259390 in which an ethylenically unsaturated compound is contacted with a liquid medium comprising a carboxylic acid and a free heteropolyacid of molybdenum or tungsten. This process is a homogeneous process in which the heteropolyacid catalyst is unsupported. A further process for producing esters is described in JP-A-05294894 in which a lower fatty acid is esterified with a lower olefin to form a
10 lower fatty acid ester. In this document, the esterification reaction is carried out in the gaseous phase in the presence of a catalyst consisting of at least one heteropolyacid salt of a metal eg Li, Cu, Mg or K, being supported on a carrier. The heteropolyacid used is phosphotungstic acid and the carrier described is silica. One of the problems with this process is that impurities present in the reactants and
15 any inert gases used in the reaction have a tendency to deactivate the acid catalyst. In particular, presence of metallic or metal compound impurities such as eg iron, chromium, molybdenum and nickel arising from the corrosion of equipment and sodium/potassium (if present in significant amounts) or calcium from any water or acetic acid reactant used are detrimental to the heteropolyacid catalyst. These
20 impurities may contaminate the catalyst either by entrainment in the vapour streams or as gas phase acetate salts in the vapour stream.

It has now been found that the process efficiency can be improved significantly by using a gaseous feedstock substantially free of such impurities.

Accordingly, the present invention is a process for the production of lower
25 aliphatic esters said process comprising reacting a lower olefin with a saturated

lower aliphatic mono-carboxylic acid in the vapour phase in the presence of a heteropolyacid catalyst characterised in that the feedstock is rendered substantially free of metallic or metal compound impurities substances prior to being brought into contact with the heteropolyacid catalyst.

5 By the expression "substantially free of metallic or metal compound impurities" is meant here and throughout the specification that the total feed to the reactor has no more than 0.1 ppm of metals and/or metal compounds, preferably less than 0.01 ppm, prior to being brought into contact with the catalyst so as to enhance acceptable catalyst life.

10 The metallic and metal compound impurities in particular are detrimental to the acid catalyst and cause deactivation. Specific examples of such impurities include the metals iron, chromium, nickel, sodium, potassium and calcium and compounds thereof. Impurities such as iron, chromium, molybdenum or nickel usually arise from the corrosion of equipment whereas those of sodium, potassium
15 or calcium result from any water or acetic acid reactant used in the reaction. In particular, these have a tendency to build up in recycle streams, especially in the acid recycle because they are carried over in the vaporiser.

These impurities may be removed from the feed to the reactor by a suitable design of the vaporiser and/or by the use of guard beds. The vaporiser may be
20 designed to minimise carry over of these metallic impurities by using demister pads and/or using a heavy ends take-off at the base of the vaporiser where most of the metal salts will be removed. The design of the vaporiser can be such that fresh acid, which is low in heavy metals, can be fed in at the top of the reactor to scrub out metals. This would improve the efficiency of metal removal. Where a guard
25 bed is used this could be in the form of a resin which is added to the liquid streams whether they be fresh feeds or recycle streams before these are vaporised. The guard bed suitably contains an ion-exchange resin through which the liquid streams pass so as to entrap the metallic or metal compound impurity present. Other materials which can be used as a guard bed include amorphous aluminosilicates,
30 clays, zeolites, aluminophosphates, silicoaluminophosphates, metalaluminophosphates and supported heteropolyacids. Specific examples of resins are eg Amberlyst® 15H, Purolite® CT 145 and CT 175. Since the impurities are likely to build up above the specified threshold levels in any streams being recycled to the reaction, it is essential that such streams are also passed
35 through the guard bed in order to minimise contamination of the catalyst by

adventitious entry of metal/metal compound impurities into the reactor.

In the reaction, the olefin reactant used is suitably ethylene, propylene or mixtures thereof. Where a mixture of olefins is used, the resultant product will inevitably be a mixture of esters. The source of the olefin reactant used may be a refinery product or a chemical grade olefin which invariably contains some alkanes admixed therewith. The other feedstock such as acid, water and recycle streams, in particular, may contain metal or metal compound impurities which have to be removed as described above prior to being brought into contact with the acid catalyst.

The saturated, lower aliphatic mono-carboxylic acid reactant is suitably a C1-C4 carboxylic acid and is preferably acetic acid.

The reaction may be carried out in a plurality of reactors set up in series such that the reactant gases exiting from a first reactor are fed as the feed gas to a second reactor and so on for subsequent reactors, and an aliquot of the reactant monocarboxylic acid is introduced into the feed gas to the second and subsequent reactors so as to maintain the olefin to monocarboxylic acid ratio in the feed gas to each of the second and subsequent reactors within a pre-determined range.

Thus, the mole ratio of olefin to the lower monocarboxylic acid in the reactant gases fed to the first reactor is suitably in the range from 1:1 to 18:1, preferably from 10:1 to 14:1. During the reaction, when the reactant gases come into contact with the heteropolyacid in a catalyst bed, at least some of the acid is used up to form the ester in an exothermic reaction and the mole ratio of olefin to monocarboxylic acid increases considerably from a starting ratio of 12:1 to about 30:1 in the exit gases from the final reactor. Where the reaction is carried out in a plurality of reactors set up in series, the exit gases from the first reactor are fed as the feed gas to the second reactor and the exit gases from the second reactor are fed as the feed gas to the third reactor and so on. When using such a series of reactors, the olefin to monocarboxylic acid mole ratio in the feed gas to the second and subsequent reactors is seriously depleted due to the acid being used up in the formation of the ester. This mole ratio of olefin to monocarboxylic acid is brought to the desired range by injecting further aliquots of the monocarboxylic acid to the feed gas prior to its entry into each of the second and subsequent reactors. In the case of the manufacture of ethyl acetate from ethylene and acetic acid, this range of mole ratios of ethylene to acetic acid in the reactant gases fed to the first reactor is suitably in the range from 1:1 to 18:1, preferably from 10:1 to 14:1 and that of

the feed gas to the second and subsequent reactors is suitably from 10:1 to 16:1. The addition of further aliquots of the monocarboxylic acid to the feed gas to the second and subsequent reactors should be sufficient to bring the mole ratio of the olefin to acid within this range of 10 : 1 to 16 : 1.

5 The plurality of reactors set up in series referred to above need not be a discrete set of individual reactors. The process of the present invention should work equally effectively if the reaction is carried out in one long reactor which has a plurality of catalyst beds set up in series and the acid is injected into the exit gases from the first bed to maintain the range of olefin to monocarboxylic acid
10 within the predetermined range in the second and subsequent stages. In a typical reaction it is desirable to use about four reactors set up in series although this can be reduced or increased without adversely affecting the beneficial effect of the injection of the monocarboxylic acid to the feed gas to the second and subsequent catalyst beds or reactors.

15 The reactors used in this context are suitably run under adiabatic conditions. Due to the exothermic nature of the reaction, it may be necessary to cool the feed gases to the second and subsequent reactors so as to maintain the reaction temperature within the desired range. This cooling may be achieved either by inserting an intermediate cooling step between the each of the reactors and can
20 be wholly or partially replaced by the injection of the acid into the feed gas to the second and subsequent reactors. The intermediate cooling step can also be used where a single long reactor which has a plurality of catalyst beds set up in series is used. In this latter case, the intermediate cooling step is used to cool the reactant gases entering the second and subsequent catalyst beds. Where a cooling step is
25 used, this may be achieved eg by using one or more of heat exchanger tubes and by injection of the additional monocarboxylic acid reactant into the feed gases as described above.

 The process of the present invention can be improved further by the addition of water as a component of the reaction mixture. The water added to the
30 reaction mixture is suitably present in the form of steam and is capable of generating a mixture of esters and alcohols in the process. It has been found that the presence of water in the reaction mixture in an amount of 1-10 mole %, preferably from 1 to 7 mole %, eg 1 to 5 mole %, based on the total feed enhances the stability of the catalyst and thereby enhances the efficiency of the process.
35 Furthermore, the presence of water also reduces the selectivity of the process to

undesired by-products such as eg oligomers and other unknowns, excluding diethyl ether and ethanol. Water addition may also be used to supplement the cooling of the feed gases to the second and subsequent reactors.

It has further been found that dosing the reaction mixture with amounts of a di-ether such as eg diethyl ether, as a co-feed also reduces the formation of undesirable by-products. The amount of di-ether co-fed is suitably in the range from 0.1 to 6 mole %, preferably in the range from 1 to 3 mole % based on the total reaction mixture comprising the olefin, the aliphatic carboxylic acid, water and diethyl ether. The di-ether co-fed may correspond to the by product di-ether from the reaction generated from the reactant olefin. Where a mixture of olefins is used, eg a mixture of ethylene and propylene, the di-ether may in turn be an unsymmetrical di-ether. The di-ether co-feed may thus be the by-product of the reaction which by-product is recycled to the reaction mixture.

The term "heteropolyacid" as used herein and throughout the specification in the context of the catalyst is meant to include the free acids. The heteropolyacids used to prepare the esterification catalysts of the present invention therefore include *inter alia* the free acids and co-ordination type partial acid salts thereof in which the anion is a complex, high molecular weight entity. Typically, the anion comprises 2-18 oxygen-linked polyvalent metal atoms, which are called peripheral atoms. These peripheral atoms surround one or more central atoms in a symmetrical manner. The peripheral atoms are usually one or more of molybdenum, tungsten, vanadium, niobium, tantalum and other metals. The central atoms are usually silicon or phosphorus but can comprise any one of a large variety of atoms from Groups I-VIII in the Periodic Table of elements. These include, for instance, cupric ions; divalent beryllium, zinc, cobalt or nickel ions; trivalent boron, aluminium, gallium, iron, cerium, arsenic, antimony, phosphorus, bismuth, chromium or rhodium ions; tetravalent silicon, germanium, tin, titanium, zirconium, vanadium, sulphur, tellurium, manganese nickel, platinum, thorium, hafnium, cerium ions and other rare earth ions; pentavalent phosphorus, arsenic, vanadium, antimony ions; hexavalent tellurium ions; and heptavalent iodine ions. Such heteropolyacids are also known as "polyoxoanions", "polyoxometallates" or "metal oxide clusters". The structures of some of the well known anions are named after the original researchers in this field and are known eg as Keggin, Wells-Dawson and Anderson-Evans-Perloff structures.

Heteropolyacids usually have a high molecular weight eg in the range from 700-8500 and include dimeric complexes. They have a relatively high solubility in polar

solvents such as water or other oxygenated solvents, especially if they are free acids and in the case of several salts, and their solubility can be controlled by choosing the appropriate counter-ions. Specific examples of heteropolyacids that may be used as the catalysts in the present invention include:

5	12-tungstophosphoric acid	-	$H_3[PW_{12}O_{40}].xH_2O$
	12-molybdophosphoric acid	-	$H_3[PMo_{12}O_{40}].xH_2O$
	12-tungstosilicic acid	-	$H_4[SiW_{12}O_{40}].xH_2O$
	12-molybdosilicic acid	-	$H_4[SiMo_{12}O_{40}].xH_2O$
	Potassium tungstophosphate	-	$K_6[P_2W_{18}O_{62}].xH_2O$
10	Sodium molybdophosphate	-	$Na_3[PMo_{12}O_{40}].xH_2O$
	Ammonium molybdodiphosphate	-	$(NH_4)_6[P_2Mo_{18}O_{62}].xH_2O$
	Sodium tungstosilicate	-	$Na_4[NiW_6O_{24}H_6].xH_2O$
	Ammonium molybdodicobaltate	-	$(NH_4)[Co_2Mo_{10}O_{36}].xH_2O$
	Cesium hydrogen tungstosilicate	-	$Cs_3H[SiW_{12}O_{40}].xH_2O$
15	Potassium molybdodivanado phosphate	-	$K_5[PMoV_2O_{40}].xH_2O$

The heteropolyacid catalyst whether used as a free acid or as a partial acid salt thereof is suitably supported, preferably on a siliceous support. The siliceous support is suitably in the form of extrudates or pellets.

The siliceous support used can be derived from an amorphous, non-porous synthetic silica especially fumed silica, such as those produced by flame hydrolysis of $SiCl_4$. Specific examples of such siliceous supports include Support 350 made by pelletisation of AEROSIL® 200 (both ex Degussa). This pelletisation procedure is suitably carried out by the process described in US Patent 5,086,031 (see especially the Examples) and is incorporated herein by reference. Such a process of pelletisation or extrusion does not involve any steam treatment steps and the porosity of the support is derived from the interstices formed during the pelletisation or extrusion step of the non-porous silica. The silica support is suitably in the form of pellets or beads or are globular in shape having an average particle diameter of 2 to 10 mm, preferably 4 to 6 mm. The siliceous support suitably has a pore volume in the range from 0.3-1.2 ml/g, preferably from 0.6-1.0 ml/g. The support suitably has a crush strength of at least 2 Kg force, suitably at least 5 Kg force, preferably at least 6 Kg and more preferably at least 7 Kg. The crush strengths quoted are based on average of that determined for each set of 50 beads/globules on a CHATTILLON tester which measures the minimum force necessary to crush a particle between parallel plates. The bulk density of the support is suitably at least 380 g/l, preferably at least 440 g/l.

The support suitably has an average pore radius (prior to use) of 10 to 500Å preferably an average pore radius of 30 to 100Å.

In order to achieve optimum performance, the siliceous support is suitably free of extraneous metals or elements which might adversely affect the catalytic activity of the system. The siliceous support suitably has at least 99% w/w purity, ie the
5 impurities are less than 1% w/w, preferably less than 0.60% w/w and more preferably less than 0.30% w/w.

Other pelleted silica supports are the Grace 57 and 1371 grades of silica. In particular, Grace 57 grade silica has a bulk density of about 0.4 g/ml and a surface area
10 in the range of 250-350 m²/g. Grace silica grade No. 1371 has an average bulk density of about 0.39 g/ml, a surface area of about 500-550 m²/g, an average pore volume of about 1.15 ml/g and an average particle size ranging from about 0.1-3.5 mm. These pellets can be used as such or after crushing to an average particle size in the range from 0.5-2 mm and sieving before being used as the support for the heteropolyacid
15 catalyst.

The impregnated support is suitably prepared by dissolving the heteropolyacid, which is preferably a tungstosilicic acid, in eg distilled water, and then adding the support to the aqueous solution so formed. The support is suitably left to soak in the acid solution for a duration of several hours, with periodic manual stirring, after which
20 time it is suitably filtered using a Buchner funnel in order to remove any excess acid.

The wet catalyst thus formed is then suitably placed in an oven at elevated temperature for several hours to dry, after which time it is allowed to cool to ambient temperature in a desiccator. The weight of the catalyst on drying, the weight of the support used and the weight of the acid on support was obtained by deducting the latter
25 from the former from which the catalyst loading in g/litre was determined.

Alternatively, the support may be impregnated with the catalyst using the incipient wetness technique with simultaneous drying on a rotary evaporator.

This supported catalyst (measured by weight) can then be used in the process of the invention. The amount of heteropolyacid deposited/impregnated on
30 the support for use in the reaction is suitably in the range from 10 to 60% by weight, preferably from 20 to 50% by weight based on the total weight of the heteropolyacid and the support.

The reaction is carried out in the vapour phase suitably above the dew point of the reactor contents comprising the reactant acid, any alcohol formed *in situ*, the product ester and water as stated above. Dew point is the temperature at
35

which condensation of a vapour of a given sample in air takes place. The dew point of any vaporous sample will depend upon its composition. The supported heteropolyacid catalyst is suitably used as a fixed bed in each reactor which may be in the form of a packed column. The vapours of the reactant olefins and acids are passed over the catalyst suitably at a GHSV in the range from 100 to 5000 per hour, preferably from 300 to 2000 per hour.

The reaction is suitably carried out at a temperature in the range from 150-200°C within which range the entry temperature of the reactant gases is suitably from 160-180°C and the temperature of the exit gases from each reactor is suitably 170-200°C. The reaction pressure is suitably at least 400 KPa, preferably from 500-3000 Kpa, more preferably about 1000 Kpa depending upon the relative mole ratios of olefin to acid reactant and the amount of water used.

The products of the reaction are recovered by eg fractional distillation. The esters produced, whether singly or as mixture of esters, may be hydrolysed to the corresponding alcohols or mixture of alcohols in relatively high yields and purity.

The process of the present invention is particularly suited to making ethyl acetate from ethylene and acetic acid by an addition reaction with optional recycle of any ethanol or diethyl ether formed.

The present invention is further illustrated with reference to the following Examples:

EXAMPLES:

In the examples STY is the space time yield measured in g EtAc/l catalyst/hour

Catalyst Preparation:

Silica pellets (Grace 57 grade, surface area 310 m²/g, bulk density 0.4 g/ml, pore volume 1.03 ml/g, ca. 5-8 mm, 9.3 kg, ex W R Grace) were soaked in a solution of silicotungstic acid [H₄SiW₁₂O₄₀.26H₂O] (32 kg of 26% w/w aqueous solution) in order to impregnate the silica support with the silicophosphoric acid catalyst. After this duration, excess catalyst solution was drained off. The resultant catalyst impregnated support pellets were then dried using a warm nitrogen stream to give a catalyst with a loading of 140 g/litre.

Catalyst Testing:

Three reactors, designed to simulate an adiabatic operation, were set up in series with intercoolers. The feedstream was heated in a vaporiser and passed into

the top of the first reactor at 176°C and 1000Kpa pressure. The exit gases from the top reactor were cooled and fed into the second reactor at 172°C and the exist gases from this second reactor were cooled and fed into a third reactor at 168°C. The exit gases from the third reactor were cooled and passed into a vapour-liquid separator at 30°C. The vapour stream from the separator was compressed and recycled to the vaporiser. The liquid stream from the separator was reduced in pressure to atmospheric and samples were analysed by gas chromatography. The feed to the first reactor was made up of fresh and recycled components made up of ethylene (3690 g/hr), acetic acid (558 g/hr), water (147 g/hr), ethanol (EtOH, 6 g/hr), diethyl ether (28 g/hr) and ethyl acetate (EtAc,113 g/hr). The three reactors were charged with 283g, 430g and 554g respectively of the silicotungstic acid catalyst specified above.

After the initial settling in period the catalyst activity was monitored by overall STY and exotherm on the three beds.

Example 1

For the period 200 - 400 hrs on stream the fresh acid/water feed contained 2.9 ppm calcium. Catalyst deactivation, particularly of the top bed was observed as outlined in the table below.

Time on stream	Overall STY	Exotherm on top bed
(hrs)	(g EtAc/lcat/hr)	(°C)
200	227	10.6
300	220	6.5
400	211	2.4

After this period the top bed of catalyst was removed and analysed. An average calcium level of 0.14 %w/w was found.

Example 2

The top bed was replaced with fresh catalyst and a further 200hour period monitored. The fresh acid/water feed now contained 0.6ppm calcium.

Time on stream	Overall STY	Exotherm on top bed
(hrs)	(g EtAc/lcat/hr)	(°C)
650	212	12.4
850	209	10.6

Again the catalyst deactivated but at a substantially lower rate than in Example 1. Analysis of the catalyst gave a calcium level of <0.01 %w/w.

Example 3

This example demonstrates the removal of metal ions from the feed stream.

5 An acetic acid stream at 78°C and containing 17.wt% water, 7wt% EtAc and 4wt% EtOH were passed through a 20 cm³ Purolite® CT145 cation resin bed at a flow rate of 190 mls/hour.. The liquid entering this resin bed contained transition metals simulating the presence of corrosion metals at concentrations of 40 ppm iron, 10 ppm nickel and 10 ppm chromium.

10 This bed removed these corrosion metals to a concentration of less than 0.1ppm (detection limit of the analysis method) and treated 11 kgs of feed prior to regeneration.

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